



# PATENT SPECIFICATION

NO DRAWINGS

1.021.400

Date of Application and filing Complete Specification: May 14, 1964.

No. 20193/64.

Application made in France (No. 934,974) on May 15, 1963.

Complete Specification Published: March 2, 1966.

© Crown Copyright 1966.

Index at acceptance:—C3 P(6A, 6C14A, 6C20B, 6D1, 6K9, 6T2D, 6T2X, 7A, 7C14A, 7C20B, 7D1A, 1D2A1, 7K9, 7T2D, 7T2X, 9A, 9C14A, 9C20B, 9D1A1, 9K6, 9K7, 9T2D, 9T2X); A5 B34

Int. Cl.:—C 08 f // A 61 k

## COMPLETE SPECIFICATION

### Polymer Products suitable for use in the Treatment of the Hair and Compositions containing them

We, L'OREAL, a French Body Corporate, of 14 rue Royale, Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polymeric products useful in cosmetics and in the treatment of the hair, to processes for their preparation and to compositions containing them.

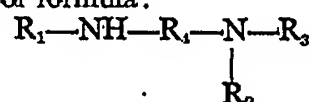
Among the substances at present employed as fixatives or setting agents for hair are derivatives of copolymers of maleic anhydride and an ethylenic monomer such as ethylene. However, these products suffer from the disadvantage that they have little affinity for the keratin which constitutes the hair, so that the hair lacquers containing them do not adhere well and are rapidly removed under the mechanical actions to which the hair is subjected. Consequently, the sets produced with these setting agents are not as durable as could be desired.

It has now been found according to the present invention that certain new derivatives of maleic anhydride - ethylenic copolymers, having a chemical structure such that they have an affinity for keratin, are most satisfactory for use in hair-setting agents. These substances also act on the hair as softening agents which impart to it a greater sliding power, whereby its appearance is improved and combing is greatly facilitated.

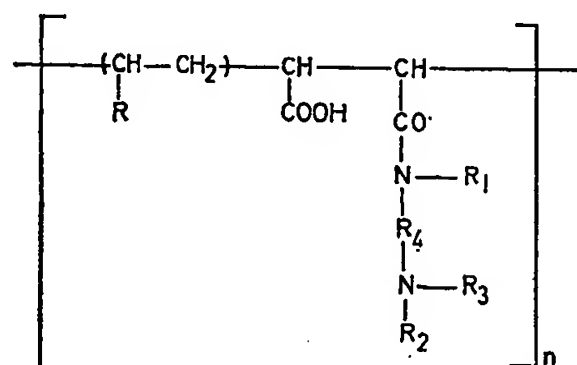
The new polymeric products of this invention are prepared by a process which comprises reacting a copolymer of maleic anhydride and an ethylenic monomer in which the molar ratio of ethylenic monomer: maleic anhydride is from 1:1 to 1:0.7, with a polyamine having a primary or secondary amine group and one or more tertiary amine groups.

The copolymer is preferably one derived from ethylene, vinylmethyl ether, vinylethyl,

ether, styrene, a halo-styrene, or a styrene homologue, as the ethylenic monomer, and a polyamine of formula:



where  $R_1$  is a hydrogen atom or an alkyl radical of 1—4 carbon atoms;  $R_2$  is an alkyl radical of 1—4 carbon atoms;  $R_4$  is an alkylene radical having 2 to 6 carbon atoms, preferably a 1,2 - ethylene, 1,2 - propylene, 1,3 - propylene or 1,4 - butylene radical; and  $R_3$  is an alkyl radical of 1—4 carbon atoms or a radical of the formula  $-R_4-N-(R_2)_2$ , where  $R_4$  and  $R_2$  have the values given above. When the ethylenic monomer is ethylene, vinylmethyl ether, vinylethyl ether, or styrene, and the polyamine has the aforesaid formula, the copolymer is believed to have the formula:—



in which  $R$  is hydrogen or a methoxy, ethoxy or a phenyl radical and  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are as hereinbefore defined.

The polyamine used in the process of the invention can be a primary - tertiary amine, for instance  $N,N$  - dimethyl - 1,2 - ethylenediamine,  $N,N$  - diethyl - 1,2 - ethylenediamine,  $N,N$  - dimethyl - 1,3 - propylenediamine,  $N,N$  - diethyl - 1,3 - propylenediamine,  $N,N$  - dipropyl - 1,3 - propylenediamine,  $N$  - propyl -  $N$  - methyl - 1,3 -

propylenediamine or *N,N* - dimethyl - 1,4 - butylenediamine; or a secondary tertiary amine, for instance *N,N* - dimethyl - *N'* - methyl-ethylenediamine or *N,N* - dimethyl - *N'* - methylpropylenediamine.

The process of the present invention may be carried out in the homogeneous phase by using as reaction medium a common solvent for the starting copolymer, for the polyamine and for the polymeric product though, of course, the solvent must not be one which would react with those substances. Suitable solvents are acetone, dioxan and pyridine.

The process can alternatively be carried out in heterogeneous medium by dropping the anhydride copolymer in small portions and with good stirring into an aqueous solution of the polyamine.

It is preferable to use proportions of copolymer and polyamine such that the primary and secondary amine groups and the anhydride functions of the polymer are in equimolecular proportions. In this way excellent yields, for example about 80%, can be obtained.

There may be added to the reaction mixture other products which react with the anhydride function, for instance a primary or secondary amine or an alcohol. Where this is done it is recommended, in order that the reaction may take place with a good yield, to add to the mixture of reactants in addition to the primary or secondary amine or the alcohol a tertiary amine in chemicals equivalent quantity.

The polymeric products of the process of the present invention can be used as setting agents, for example in solution at concentrations between 0.5% and 6%, especially between 2% and 5% by weight, in water or in aqueous alcohol. They are also of use in cosmetic gels or creams as thickening agents.

The invention is illustrated by the following Examples.

#### EXAMPLE 1

Into 250 cc. of a 2% solution of *N,N* - dimethyl - 1,2 - ethylenediamine in water there is dropped in small successive portions, and with vigorous stirring, 8.85 g. of a copolymer of equimolar proportions of methylvinyl ether and maleic anhydride, care being taken that each successive portion of the copolymer is dropped only when the preceding portion has been completely dissolved in the amine solution. To the resulting viscous solution there is added a mixture of equal proportions of alcohol and ethyl acetate which precipitates a solid polymeric product.

The product of the reaction may be used as a softening agent by introducing it into a shampoo in a proportion of 0.5% by weight. The shampoo thus treated provides a lather which is particularly soft to the touch and imparts to the hair high gloss and suppleness.

The product of this Example may also be

employed as a thickening agent for cosmetics, preferably in a concentration of about 2% by weight.

#### EXAMPLE 2

To 250 cc. of a 10% solution of *N,N* - diethyl - 1,3 - propylene - diamine in acetone are added 250 cc. of an acetone solution containing 9.6% of an ethylene - maleic anhydride copolymer (molecular ratio 1:1). It is observed that the reaction starts by itself with evolution of heat, and it is then sufficient to complete it by heating. The solvent is then removed from the resulting solution by evaporation, leaving as residue a polymeric product.

The product obtained may be successfully used as a softening agent for setting lotions by dissolving it in a proportion of 3% by weight in 30% aqueous solution of ethyl alcohol. The resulting solution has a low viscosity if the starting copolymer is itself of low viscosity.

#### EXAMPLE 3

To 100 cc. of an aqueous solution containing 6% of *N,N* - dimethyl - 1,3 - propylenediamine, 4% of butylamine and 4.2 g. of pyridine is added in small quantities 14.3 g. of a copolymer of equimolecular proportions of ethylene and maleic anhydride, care being taken, before each successive portion of copolymer is added, that the preceding portion has been completely dissolved.

The solution thus obtained may be directly employed or the reaction product may be separated by evaporation and washing with alcohol so as to eliminate any unreacted amine. The polymeric product thus obtained may be employed in solution in water or in an aqueous alcohol as a setting lotion. The concentration of polymeric product in such solutions may be, for example, from 2% to 5% by weight, the lotion containing, for example, 25% by weight of alcohol.

#### EXAMPLE 4

18 g. of a copolymer resulting from the copolymerisation of 104 g. of styrene (1 mol) and 88 g. of maleic anhydride (0.9 mol) are reacted with 100 cc. of an aqueous solution containing 10% of *N,N* - diethylethylene - diamine, the copolymer being added in small successive portions and care being taken to ensure that each successive portion has dissolved before the next portion is added. The solution thus obtained may be employed in combination with the products obtained in accordance with Examples 2 and 3, for the same purposes and in the previously indicated concentrations. For example, it is possible to obtain an excellent setting lotion by introducing into a 20% by weight aqueous solution of ethyl alcohol 0.5% by weight of the product of this Example and 1.5% by weight of the product of Example 3.

#### WHAT WE CLAIM IS:—

1. A process for the preparation of polymeric

- products suitable for use in setting agents for human hair, which comprises reacting a copolymer of maleic anhydride and an ethylenic monomer, in which the molar ratio of ethylenic monomer: maleic anhydride is from 1:1 to 1:0.7, with a polyamine having a primary or secondary amine group and one or more tertiary amine groups.
- 5 2. A process according to claim 1, in which the poly-amine has the formula:—
- $$\begin{array}{c}
 R_1-NH-R_3-N-R_3 \\
 | \\
 R_2
 \end{array}$$
- 10 where  $R_1$  is a hydrogen atom or an alkyl radical of 1—4 carbon atoms;  $R_2$  is an alkyl radical of 1—4 carbon atoms;  $R_4$  is an alkylene radical having 2 to 6 carbon atoms; and  $R_3$  is an alkyl radical of 1—4 carbon atoms or a radical of the formula
- $$-R_4-N-(R_2)_2,$$
- 15 where  $R_1$  and  $R_2$  have the values given above.
- 20 3. A process according to claim 1 or 2, in which the ethylenic monomer of the copolymer is ethylene, vinylmethyl ether, vinyl-ethyl ether, styrene, a halo-styrene, or a styrene homologue.
- 25 4. A process according to claim 2 or 3, in which the copolymer is one which has been prepared by the copolymerisation of the monomers in substantially equimolar proportions.
- 30 5. A process according to claim 2, 3 or 4, in which  $R_4$  is a 1,2 - ethylene, 1,2 - propylene, 1,3 - propylene or 1,4 - butylene radical.
- 35 6. A process according to any of the preceding claims, in which the polyamine is  $N,N$ -dimethyl - 1,2 - ethylenediamine,  $N,N$ -diethyl - 1,2 - ethylenediamine,  $N,N$ -dimethyl - 1,3 - propylenediamine,  $N,N$ -diethyl - 1,3 - propylenediamine,  $N,N$ -diethyl - 1,3 - propylenediamine,  $N$ -propyl- $N$ -methyl - 1,3 - propylenediamine or
- 40  $N,N$ -dimethyl - 1,4 - butylene - diamine.
7. A process according to any of claims 1 to 5, in which the polyamine is  $N,N$ -dimethyl- $N^1$ -methylethylenediamine or  $N,N$ -dimethyl -  $N^1$ -methylpropylenediamine.
- 45 8. A process according to any of the preceding claims, in which the copolymer and polyamine are used in amounts such that they contain respectively substantially equimolar proportions of anhydride rings and primary or secondary amine groups.
- 50 9. A process according to any of the preceding claims, in which a primary or secondary amine or an alcohol which will react with the anhydride function of the copolymer is present in the reaction mixture.
- 55 10. A process according to any of the preceding claims, in which the reaction is carried out in the homogeneous phase in a common solvent for the starting copolymer, for the amine and for the polymeric product resulting from the reaction.
- 60 11. A process according to claim 10, in which the reaction medium is acetone, dioxan or pyridine.
- 65 12. A process according to any of claims 1 to 9, in which the reaction is carried out in a heterogeneous medium, the copolymer being added in small portions to an aqueous solution of the amine.
- 70 13. A process according to claim 1, substantially as described herein.
- 75 14. Polymeric products suitable for use in compositions for treatment of the human hair, when obtained by the process of any of the preceding claims.
- 80 15. A composition for treating human hair, which comprises a solution of from 0.5% to 6% by weight of a compound claimed in claim 14 dissolved in water or in an aqueous alcoholic solution.
- 85 16. A composition according to claim 15, in which the amount of the said compound is from 2 to 5% by weight.
- 90 17. A cosmetic composition in the form of a gel or cream, which contains as a thickening agent a product claimed in claim 14.
18. A method of treating human hair, which comprises applying to the hair a product claimed in claim 14 or a composition claimed in claim 15 or 16.
- J. A. KEMP & CO.,  
Chartered Patent Agents,  
14 South Square,  
Gray's Inn, London, W.C.1.